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Part III

MORPHOLOGICAL STUDIES OF POLYETHYLENE TEREPHTHALATE

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ABSTRACT

The morphology of polyethylene terephthalate has been studied by electron microscopy. The morphology of the glassy state is characterized by ball-like structures. Crystallizations from the glass occurs in spherulites similar to those obtained from the melt. Although the long period increases as measured by small angle x-ray scattering with annealing temperature, it decreases with time at a given annealing temperature.

Strain induced crystallization occurs by alignment of the ball-like structures. Subsequent heat setting of the strained material produces more complete alignment of the ball-like structures.

A special technique, low-angle electron scattering, has been developed in order to investigate the details of the morphology of polyethylene terephthalate.

I. Morphology of Unoriented PETP

Initial structural studies were directed towards defining the morphology of PETP crystallized from the melt and solution and to preparing, as a result, well characterized samples for mechanical property studies. Particularly desired, were single crystals. The latter purpose, as described below, was not satisfactorily attained; it has not yet proven possible to obtain large, reproducible samples of well defined single crystals. In as much as the solution and melt work has been, at least temporarily, stopped, the results are described in some detail. Work is still in progress in the areas of the structure of amorphous PETP and the effect of strain induced crystallization and therefore, in these areas, only brief summaries of the present status and conclusions are given.

A. Crystallization from Solution

Figure 1 shows a typical example of the type of structures obtained by crystallization from solution, both by cooling and under isothermal conditions. More than 20 different solvents were tried, over a wide range of temperatures. No significant effect of solvent or temperature was observable other than on the overall size of structures. In all cases they were spherulitic in nature, consisting of aggregates of irregular, fibrillar ribbons, each about 100 $\mathring{A}$ thick, several hundred angstroms wide and several thousand angstroms long. The size of the

spherulites varied from about 0.5 μ to 10μ, depending on the crystallization conditions. For the same solvent higher temperatures resulted in larger spherulites. The thickness of the ribbons suggests the possibility of chain folding. Ribbons of similar dimensions have been observed during the crystallization of several nylons and polyesters from solution (1) and in several cases chain folding similar to that occurring in lamellar crystals of large lateral dimensions has been demonstrated by electron diffraction. Attempts to determine the chain orientation within the spherulitic ribbons of PETP were unsuccessful. Although weak diffraction patterns could be obtained from portions of a spherulite, their small size and randomness of their arrangement made the results inconclusive; further attempts were halted when it was found possible to obtain oriented arrays of the fibrils by epitaxial crystallization (see below). The structure of the fibrils obtained in this manner is believed to be the same as that in the spherulites.

Yamashita[2] has previously reported the growth of lamellar crystals of PETP by solvent evaporation. It was this work that originally led us to hope lamellar crystals could be grown in suspension. Although we have been able to grow, by solvent evaporation, lamellae similar to those reported by Yamashita, we find that the results are highly variable, with considerable variations in structure being observed even on a given slide from which the solvent has been evaporated. In general, in this and similar studies of the crystallization of polypeptides, we find solvent evaporation experiments to have poor reproducibility.

The crystals prepared by solvent evaporation in most cases had the appearance shown in Figure 2. They are quite irregular with no recognizable, crystallographic growth faces. Fibrillar overgrowths are usually present. In fact, the basal layer often appears fibrillated. The overgrowths and the structure of the basal layer suggests weak lateral cohesion within the lamellae, with the lamellae perhaps breaking down into the fibrils under hydrodynamic forces in the liquid. This would help to explain the lack of lamellar crystallization in suspension, any lamellae forming rapidly breaking up into individual fibrils while tumbling about in the solution.

In one solvent evaporation experiment only, well formed lamellae with crystallographic faces and distinguishable spiral growths were observed (Figure 3). Fibrillar material, however, was associated with each lamellar object. Similar structures have been observed during the crystallization of polyhexamethylene terephthalate in suspension[1]. In both cases the relationship between the fibrils and the lamellae is not clear. In the latter polymer the lamellae appear to grow out from the fibrils, perhaps as the solution became more dilute, whereas in PETP the relative times of growth are not known. The lamellae do not necessarily develop in contact with the substrate; in several micrographs, fibers can be seen under the lamellae. Electron diffraction patterns were not obtained from the original samples and the lack of reproducibility has prevented further study.

B. Epitaxial Crystallization

As indicated above, electron diffraction patterns from the fribrillar spherulites were of little use in determining the conformation of the chains in the fibrils. Work in this laboratory by Koutsky, Walton, and Baer[3] on epitaxial crystallization of a number of polymers on alkali halide substrates suggested this might be a way of obtaining a sufficiently large, oriented sample of the fibrils to permit photographing interpretable electron diffraction patterns. In the case of polyethylene, polyoxymethylene and a number of other polymers, crystallization from solution on alkali halides results in the nucleation and growth of lamellar crystals oriented normal to the substrate.

Under suitable conditions oriented clusters of fibrillar ribbons of PETP can be grown epitaxially on Na Cl both in solution and by solvent evaporation. An example of a sample prepared in solution, by immersion of the Na Cl crystal in a dimethyl phthalate solution at 120°C, is shown in Figure 4. The fibrils are oriented preferentially along the <110> directions of the Na Cl. As in the case of the spherulitic fibrils they are on the order of 100Å thick, several hundred to a thousand Å wide and a micron or more long. The 100Å thick edge lies in contact with the substrate (as in the case of lamellar crystals of other polymers).

It was possible to obtain satisfactory selected area electron diffraction patterns from these samples using a cold stage in the microscope. An electron diffraction pattern and the corresponding selected area is shown in the lower right of Figure 4. The strong

reflections are from $(1\bar{1}0)$ and $(1\bar{1}1)$ planes. On the originals a weak $\bar{1}05$ reflection was observed along the meridian, i.e., the $\bar{1}05$ planes are nearly perpendicular to the fiber axis. The molecular axes are in the (110) planes of the unit cell, which are parallel to the substrate. The axes of the molecules make an angle of about 56^{o} with the long axis of the fibril, requiring a chain folded conformation, suggesting a similar conformation in the spherulitic fibrils. The 56^{o} angle does not appear to be simply related to any unit cell parameter. In the triclinic unit cell the $\underline{c}$ axis is at an angle of 98.5^{o} to the $\underline{b}$ axis, the $\underline{b}\,\underline{c}$ plane containing the benzene rings which therefore lying at an angle to the substrate. The tilt of the chains by about 34^{o} from the normal to the fibril axis is believed to be more exact than that reported by Yamashita[2] in their crystals ($25\text{-}35^{o}$).

Although the diffraction patterns indicate the orientation of the unit cell with respect to the fibers axes, they do not present information concerning the fold plane orientation; models suggest the molecules may fold within the (100) or (010) planes. An attempt to determine the fold plane orientation was made by investigating the deformation characteristics of the fibrils. Epitaxially grown fibrils were floated on water and picked up on "Mylar" substrates in a small sample stretcher. As in previous single crystal deformation studies in our laboratories, the sample adheres to the Mylar and deforms as the Mylar is drawn. When the PETP fibrils are drawn they fail in a brittle fashion suggesting that the fold planes are at an angle to the substrate and must be along the $\underline{a}$ axis. If they were parallel to the substrate one would expect fibrils to be drawn across any cracks formed in the original fibrils.

(This is observed in polyethylene single crystals and epitaxially grown networks of crystals of several polymers.) This result suggests that possibly the width of the gibril is associated with the lateral size of the fold plane for one molecule. However, this result would need further study using fractionated samples of known molecular weight.

C. Crystallization of PETP from Bulk Material: Morphology of Amorphous PETP

Much of the work discussed below is still in progress and will therefore be only briefly summarized. In addition, many of the conclusions are only tentative.

As described in our previous report (see Figures 5 and 6 of Ref. 4) PETP crystallizes from the melt and the glassy state in the form of spherulites composed of lamellae. These lamellae appear to be ribbon-like and thus are presumably of similar morphology to those crystallized from solution. The spherulite size and density of nuclei (which are directly related only when the spherulites fill the volume) have been found to be strongly dependent on the previous thermal history of the sample. The small angle X-ray diffraction long period, from the samples originally quenched to a glass is found to depend primarily on the crystallization temperature and time. Although still open to question in several polymers (5) it is usually assumed that the long period is related to the lamellae thickness. Typical results are shown in Figure 5. As in other polymers crystallized from the melt the long period increases with annealing temperature for a given time of annealing (Figure 5a). (This sample was originally quenched to a glass.) However, there is found to be a decrease

in long period with time at a given annealing temperature, which is opposite the effect found for other polymers crystallized from the melt. (The effect of time on the long period of PETP crystallized from the melt has not yet been measured.) Similar results to those described above have also been obtained in Fischer's laboratory (University of Mainz). He suggests that the decrease in spacing is due to a regularizing of a previously irregular fold surface. In this case one would expect a subsequent increase in long period as the lamellae thicken. Neither he nor we have observed such an effect.

An understanding of the above effect, as well as an understanding of the physical properties of glassy PETP will require a knowledge of the "morphology" of the amorphous polymer. As reported in our previous report (4) replicas of PETP quenched to a glass from the melt indicate the presence of a structure on the 100Å size scale (see Figure 7, Ref. 4, and Figure 6 in this report) over the entire surface of the sample. Further investigations of this structure have been made using solution-case amorphous films. The same ball-like structures are observed (Figure 6). These films can be made thin enough for transmission microscopy and diffraction. The wide angle electron diffraction patterns confirm the amorphous state of the sample. The use of thin films rather than replicas permits observation of unshadowed samples. The balls are observable as regions of fair contrast even in these samples indicating a fluctuation in electron density in the sample in this size range. Although extremely difficult because of their small size, dark field microscopy studies are currently in progress. The initial results suggest there is a certain

degree of order within the particles. This order may be related to the packet structure for amorphous polymers suggested by Kargin (see Ref. 1) or our belief that the fringed micelle model is a reasonable picture for amorphous polymers; modified, however, by the probable presence of some folding.

Similar replica observations of structure in amorphous PETP were described to us by Fischer during a recent visit to his laboratory. He indicated an increase in the size of the balls (up to 600Å) could be induced by annealing below Tg, the size shrinking again if the sample is then annealed above Tg and quenched. We have to date, been unable to repeat these experiments, although some change in structure is observed following annealing below Tg. Because changes in modulus, internal friction and rate of gas absorption are affected by these changes and because of its significance with respect to the morphology of amorphous materials, this work is being continued. The balls appear to play a role in both crystallization by annealing (below) and by strain (next section).

It is suggested that the structure of the balls may be related to the decrease in long period with annealing time described above. Possibly the lamellae in the growing spherulites can be pictured as initially forming by the juxtaposition or next neighbor alignment and rotation of the balls. The balls must have some order within them, but any folds present (which would be required if molecules were primarily contained within a given ball) would be expected to be irregular. Further annealing would result in a regularizing of these folds, a decrease in the maximum fold period and resulting closer packing of the lamellae and therefore a decrease in long period.

II. Morphology of Strain-Induced Crystallization of PETP

A detailed study is being made of the strain-induced crystallites of PETP, before and after annealing at high temperatures. Standard techniques such as small and wide angle X-ray diffraction, and transmission and replication electron microscopy are the primary tools being employed. A new technique called selected area small angle electron scattering was developed especially for our present investigation. This technique is described in a separate section of this report. However, it would be appropriate to mention that the contribution of the knowledge gained in the development of this new technique has added substantially to our overall understanding of the structure of the strained-induced crystallites in PETP.

Both bulk and thin film samples were studies. Thick amorphous films (~1/16") kindly supplied by Dr. T. Serafini of NASA were required for X-ray studies. Thin films were prepared by solution casting techniques using either m-cresol or trifluoroacetic acid as the solvent. All films, including the thick ones for X-ray work, have a grainy appearance due to the presence of ball-like structures (see Figure 6). The thinner the film the more pronounced is this structure. On stretching, these ball-like structures tend to align themselves in irregular rows of 5-10 balls at a substantial angle to the draw direction (Figure 7). Figure 3 is obtained from a specimen drawn uniaxially to six times its original length at about 65°C over a water surface. The diffraction pattern from this sample is shown in the same figure. It is a highly oriented fiber pattern. On heat-setting at about 200°C, the diffraction pattern becomes more intense and higher

orders of reflections can be seen as well. (Figure 8) Results from dark field studies showed that the strain-induced crystallites are small -- on the order of the size of the balls. They do not change significantly in size even after heat-setting, retaining the form of spherical, ball-like structures throughout the sample. However, they do become more densely and uniformly packed the higher the temperature at which the sample is heat-set.

At a heat set temperature of about 260°C, the ball-like structures become so uniformly packed (Figure 9), that a small angle electron scattering pattern begins to show up as well. (See insert, Figure 9.) In this temperature range, the rows of balls, normal to the stretch direction, become quite wide. The rows are somewhat irregular and curved. The small angle pattern corresponds to a periodicity of about 200Å which agrees with the center to center distance of the ball-like structures. Samples prepared at a heat-set temperature below 260°C gave no small angle electron scattering patterns even though thick heat set samples did produce well-defined small angle X-ray patterns at similar temperatures. (See Figure 10.) These differences are still being studied. Possibly the exposure time was insufficient.

The small angle X-ray pattern of a stretched sample without heat-set gave only a faint indication of a 4-point pattern even after an exposure time of 48 hours. The typical 4-point pattern of this material tends to orient towards the meridian at higher heat-set temperatures. The origin of the 4-point diagram has been discussed by several authors.[6,7] From the morphological evidence we have presented here, it will appear

that various arrangements of these ball-like structures in oriented samples could very well result in some type of 3 dimensional network structure which will give rise to a 4-point pattern. It should be pointed out that the electron micrographs of the samples annealed at or below 250°C suggest that there is not enough regularity of packing of the balls to result in an intense small angle pattern.

In some of the thicker solution cast, stretched films it was found that lamination occurred (Figure 11). This may be the result of the crystals tending to form in a layer-like fashion, perhaps with the benzene rings parallel to the surfaces. Consequently, there could be very little cohesive forces between the layers. Work is still needed in relating this delamination to the ball-like structures, particularly since none can be seen in the laminated film.

III. Selected Area Small Angle Scattering Electrons

A new technique called selected area small angle electron scattering has been developed using a standard, double condenser electron microscope. The technique is capable of resolving spacings up to at least 2000Å from first order discrete reflections. The required, much greater camera length is accomplished by an increase in the objective focal length using a modified specimen holder. The advantage of this technique lies in the photographing of the exact selected area which gives rise to the small angle scattering in addition to the inherent capabilities of obtaining related wide angle diffraction and bright and dark field micrographs. To test this new technique a number of standard, specifically prepared specimens such as polymers with known structures, latices of uniform sizes, gold colloids, etc., were used. Results of small angle electron diffraction studies from these specimens can in most cases be explained based on the structures observed in the corresponding electron micrographs. Some questions still remain, however, concerning the relationship of the dark field micrographs which show the origin of the scattering to theory. In view of the present controversy regarding the interpretation of small angle X-ray scattering patterns, this technique shows particular promise in the overall study of the fundamental basis of small angle scattering phenomena arising from bulk and oriented polymers, as well as contributing to the theory of small angle diffraction.

Following are some examples of model specimens used in our investigation of the usefulness of this method. Figure 12 shows the typical striated structures one normally obtains on annealing of polymer fibers.[8]

The polymer employed here is polyethylene. Fibers were first obtained by shearing polyethylene single crystals between two glass slides, then annealed at 128°C for 5 hours to produce these striated structures in which the polymer chains have been shown to be folded.[8] Some remnants of the fibers can still be observed in the upper right hand corner of Figure 12. Its small angle electron diffraction pattern and corresponding selected area are shown in the insert. The striated structures measured about 350Å in width, which agreed quite well with the spacing of about 365Å calculated from their corresponding small angle pattern. Higher orders of reflections up to as many as three have been observed in some preparations. They are orders of each other, i.e., first, second, and third, and their intensities decrease in the expected manner also. Recently, some very uniform latex particles have been made by Woods and Dodge[9] in our laboratory. They can be prepared in a hexagonal, crystalline arrangement under slow drying conditions. An example is shown in Figure 13. These uniformly packed particles are each about 2000Å, which again agrees well with measurements obtained from their corresponding small angle scattering pattern (see insert of Figure 13). The small angle scattering pattern is of a single crystal type, again indicating the uniformity of the packing of these lattices. As was mentioned earlier the technique is capable of being extended to dark field microscopy using portions of the small angle diffraction pattern. Results for latex particles are demonstrated in the following figures. Figure 14 is a dark field photograph taken of some uniformly packed 1350Å latex particles by placing a small aperture over a portion of the discrete reflections shown in the same figure. Some of the individual particles seem to light up, as

well as some of the "voids", while others do not. This cannot at present be explained theoretically.

Dark field photographs from diffuse scattering such as the star pattern in Figure 15 are given in Figures 16 and 17 with their corresponding selected scatterings. Here the edges of the 12,400Å latex particles seem to contribute to the scattering observed. The discrete diffraction from these particles is at too small an angle to resolve. In other cases the diffuse scattering can be attributed to defects in the packing. Other specimens examined include gold colloids and replicas of gratings. In general, the measured spacings from small angle scatterings can be accounted for by the structures observed in the selected area of the corresponding electron micrograph. From our present studies, we conclude that one of the necessary requirements for small angle scattering to arise is there must be sufficient electron density difference in the sample. For example, in the striated structures shown in Figure 13, this requirement is fulfilled by the folding of the chains within the interfacial regions. To carry this conclusion in our present study of oriented PETP, we suggest that chain folding must also be present in order for the small angle scattering pattern to appear as shown in the insert in Figure 10. Work in this area is still in progress.

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Figure Captions

Fig. 1 Fibrillar spherulitic structures of PET crystallized isothermally from a .05% dimethyl phthalate solution at 125°C.

Fig. 2 Lamellar phatelets with fibrillar overgrowths of PET obtained on solvent evaporation from a .005% dimethyl phthalate solution in an air oven controlled at 145°C.

Fig. 3 "Spherulites" of PET obtained on solvent evaporation from a .005% dimethyl phthalate solution in an air oven controlled at 125°C. Single lamellae are seen in the same structure together with the fibrils. (Pt-C shadowed at $\tan^{-1} 4/8$)

Figs. 4 Oriented overgrowth of PET on (001) NaCl. Fibrils are seen oriented along <100>. (Pt-C shadowed at $\tan^{-1} 4/8$) Blank scale bar indicates one micron.

Lower right: Selected area diffraction pattern of oriented fibrils and its corresponding selected area. The two strong reflections are 1$\bar{1}$0 and 1$\bar{1}$1. The third reflection, a very weak one, is $\bar{1}$05. The ring is due to the Pt-C shadowing material.

Fig. 5 Variation of long period, l, with temperature and time of annealing.

Fig. 6 Solvent-cast, amorphous film of PETP showing spherical, ball-like structures.

Fig. 7 Amorphous film stretched at 65°C to obtain strain-induced crystallization.

Fig. 8 Electron diffraction pattern of sample heat-set at 200°C after strain-induced crystallization.

Fig. 9 Sample heat-set at 260°C after strain-induced crystallization.

Upper right: Its small angle electron scattering pattern.

Fig. 10 Small angle x-ray patterns of bulk samples.

Left: Stretched at 110°C.

Middle: Stretched at 110°C, heat-set at 180°C for 15 mins.

Right: Stretched at 110°C, heat-set at 200°C for 15 mins.

Fig. 11 Lamination seen in some thicker, stretched films.

Fig. 12 Striated structures seen on fibers after annealing at 128°C for 5 hours. Insert shows the small angle electron scattering pattern of this sample and its corresponding selected area.

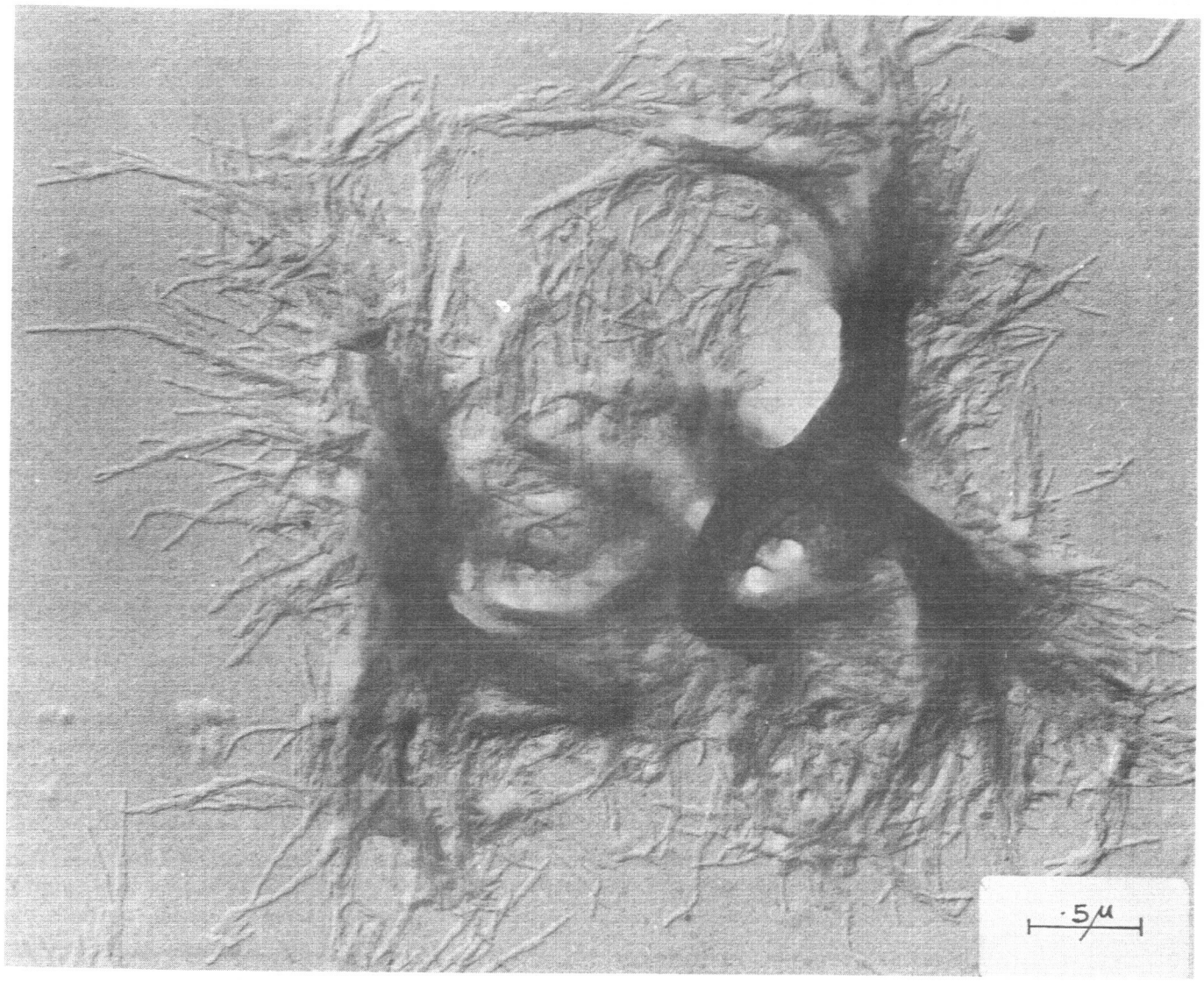
Fig. 13 Uniformly packed 2000Å latex particles and its corresponding small angle electron scattering pattern.

Fig. 14 Dark Field of 1350Å latex particles and its corresponding small angle electron scattering pattern.

Fig. 15 Diffuse scattering from 12,400Å latex particles.

Fig. 16 Dark field of 12,400Å latex particles and its corresponding selected electron scattering giving rise to the dark field picture.

Fig. 17 Same as Fig. 16, except the dark field is from a different portion of the diffuse scattering.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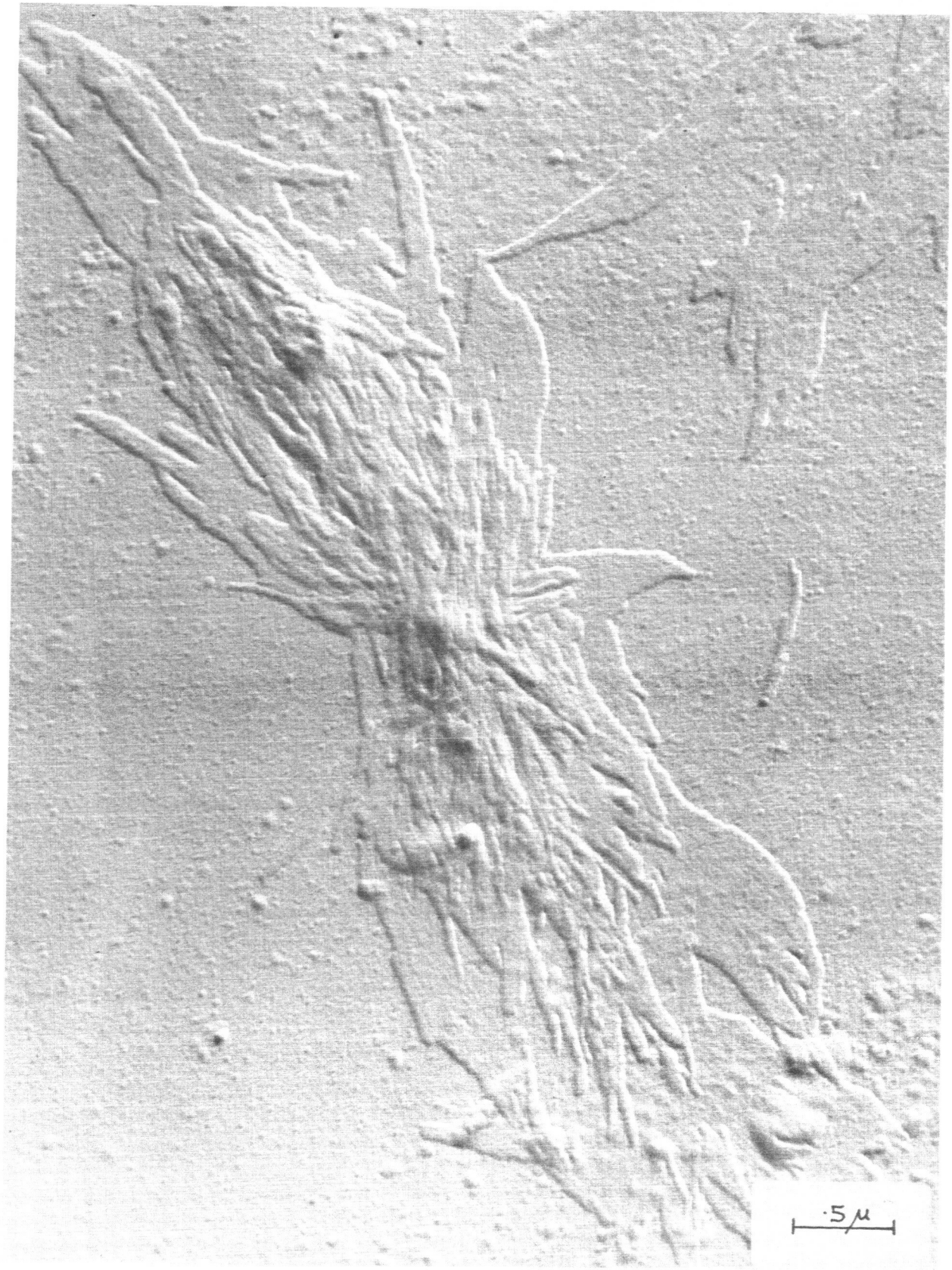
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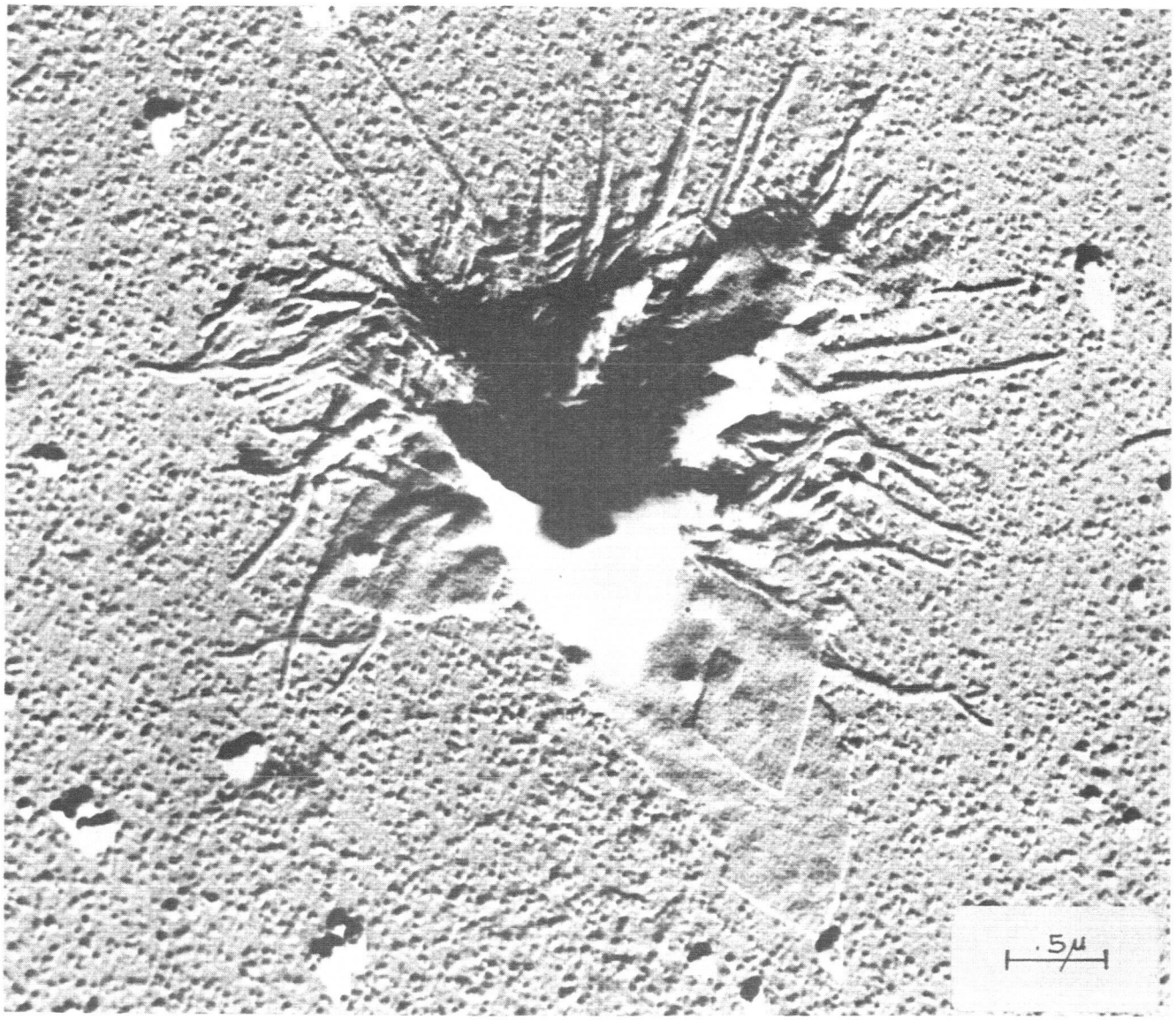
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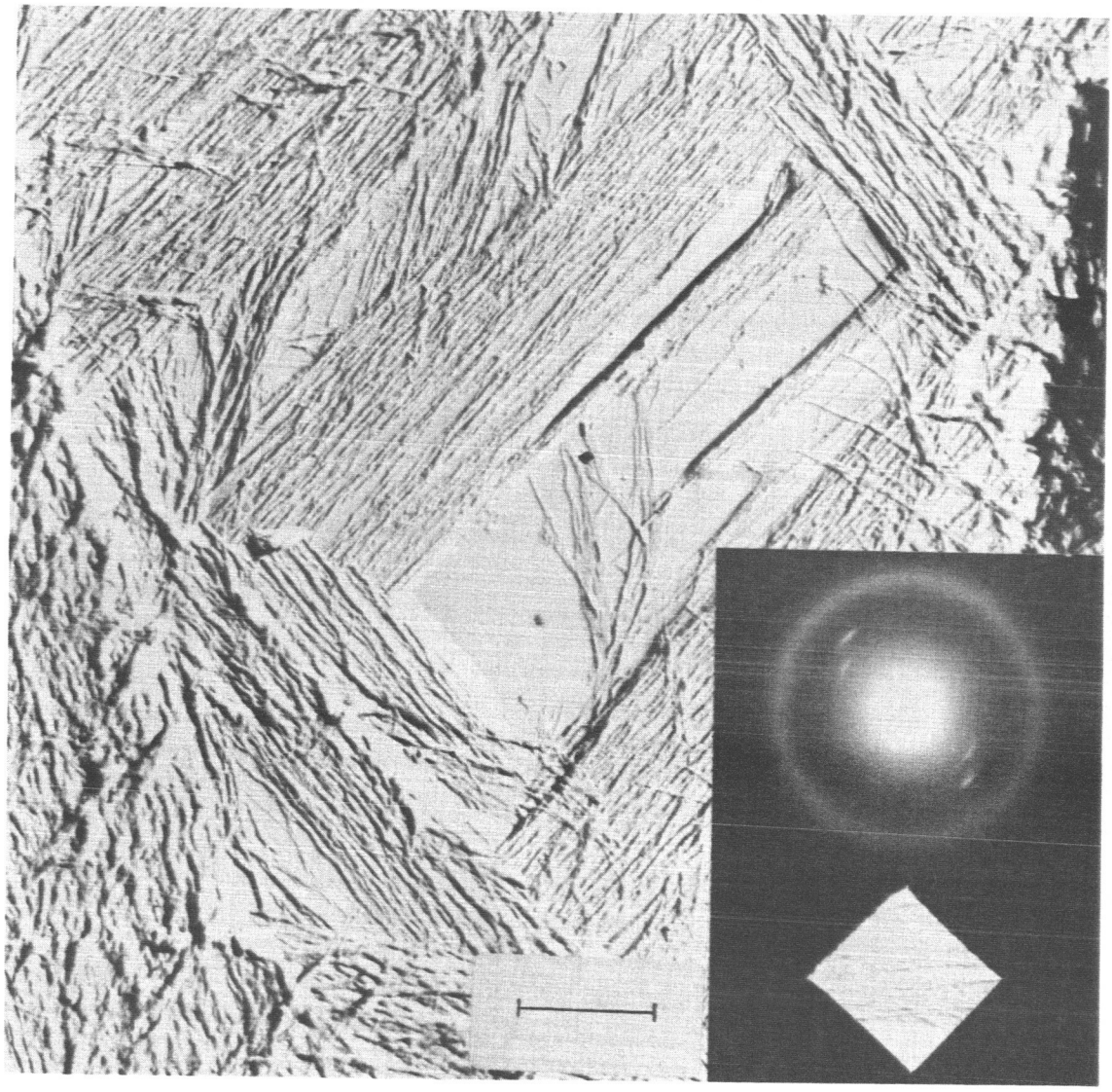
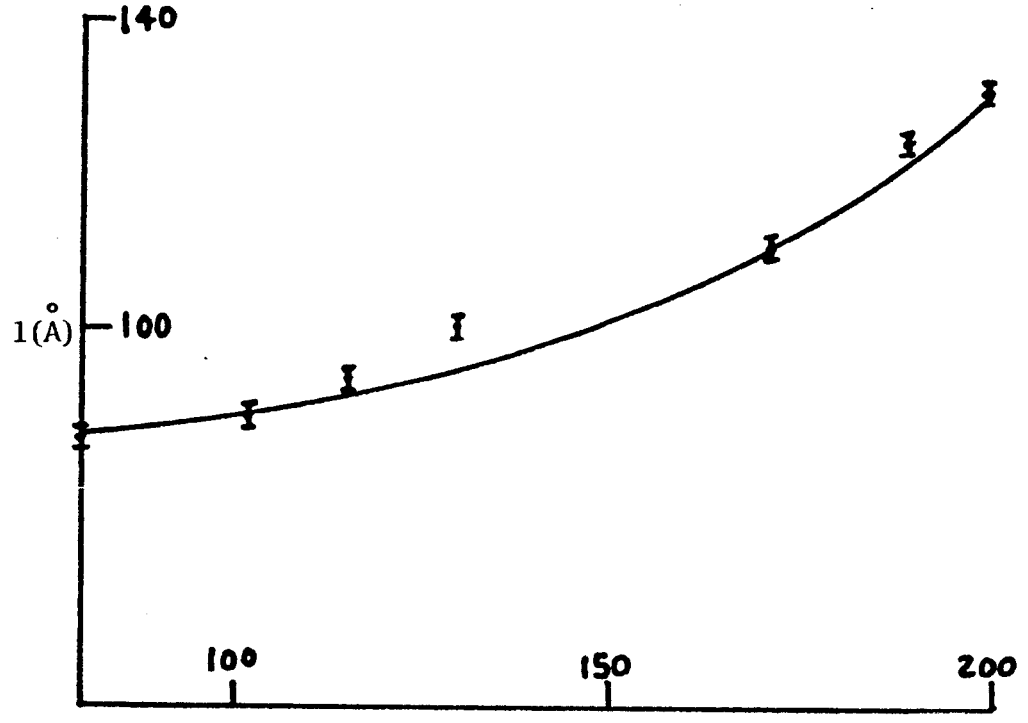
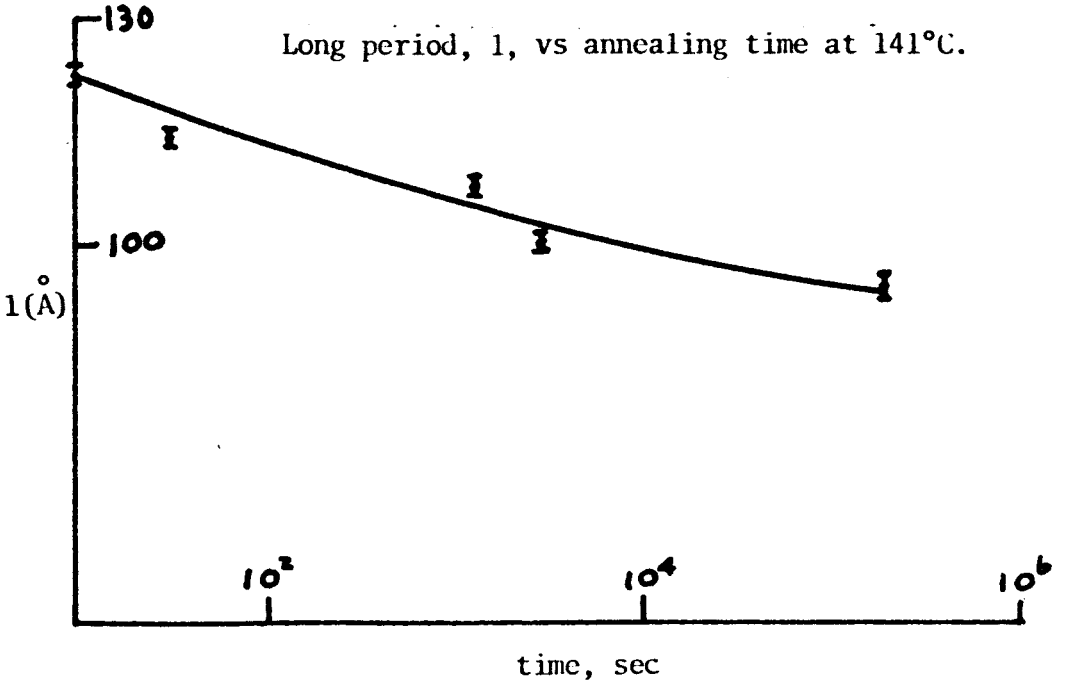
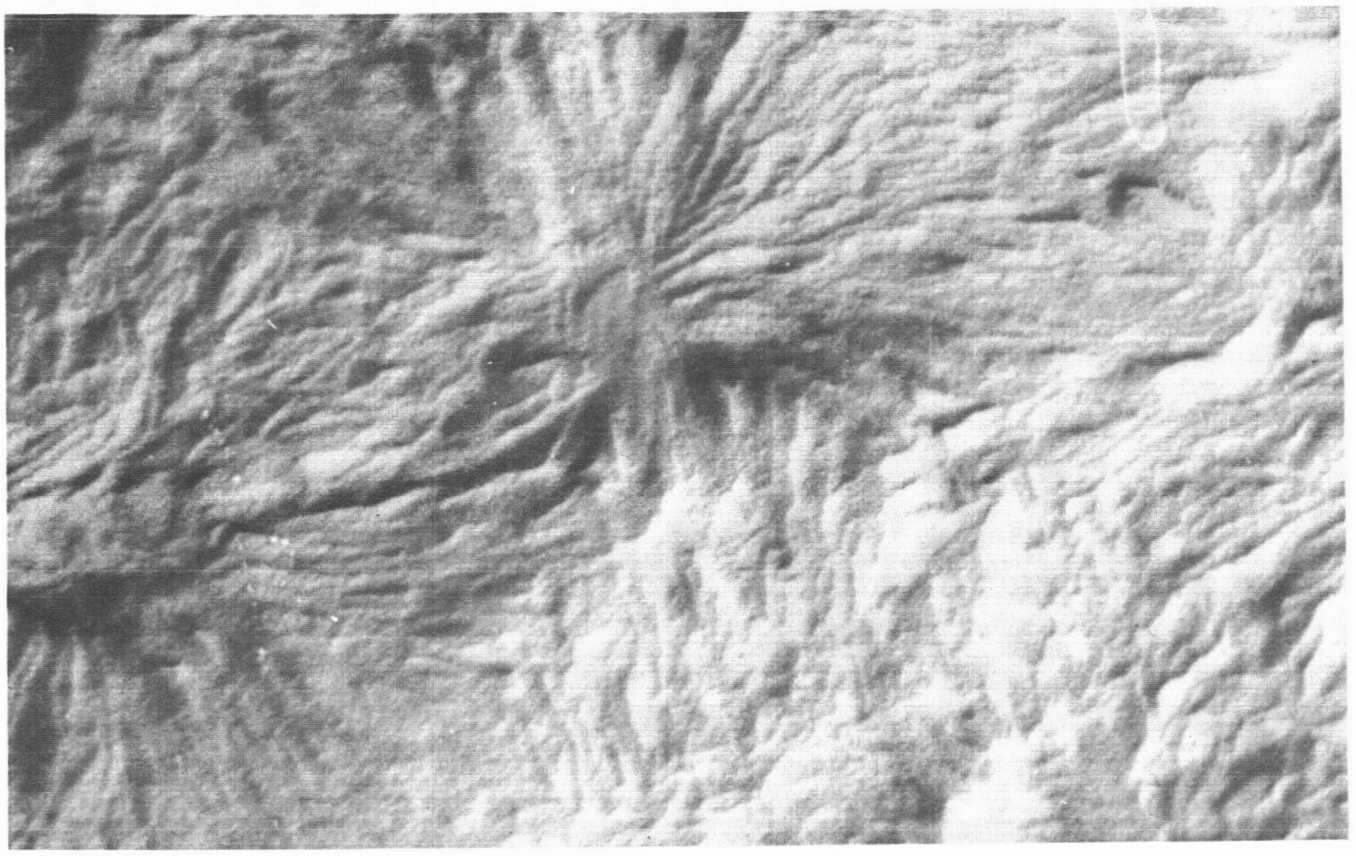


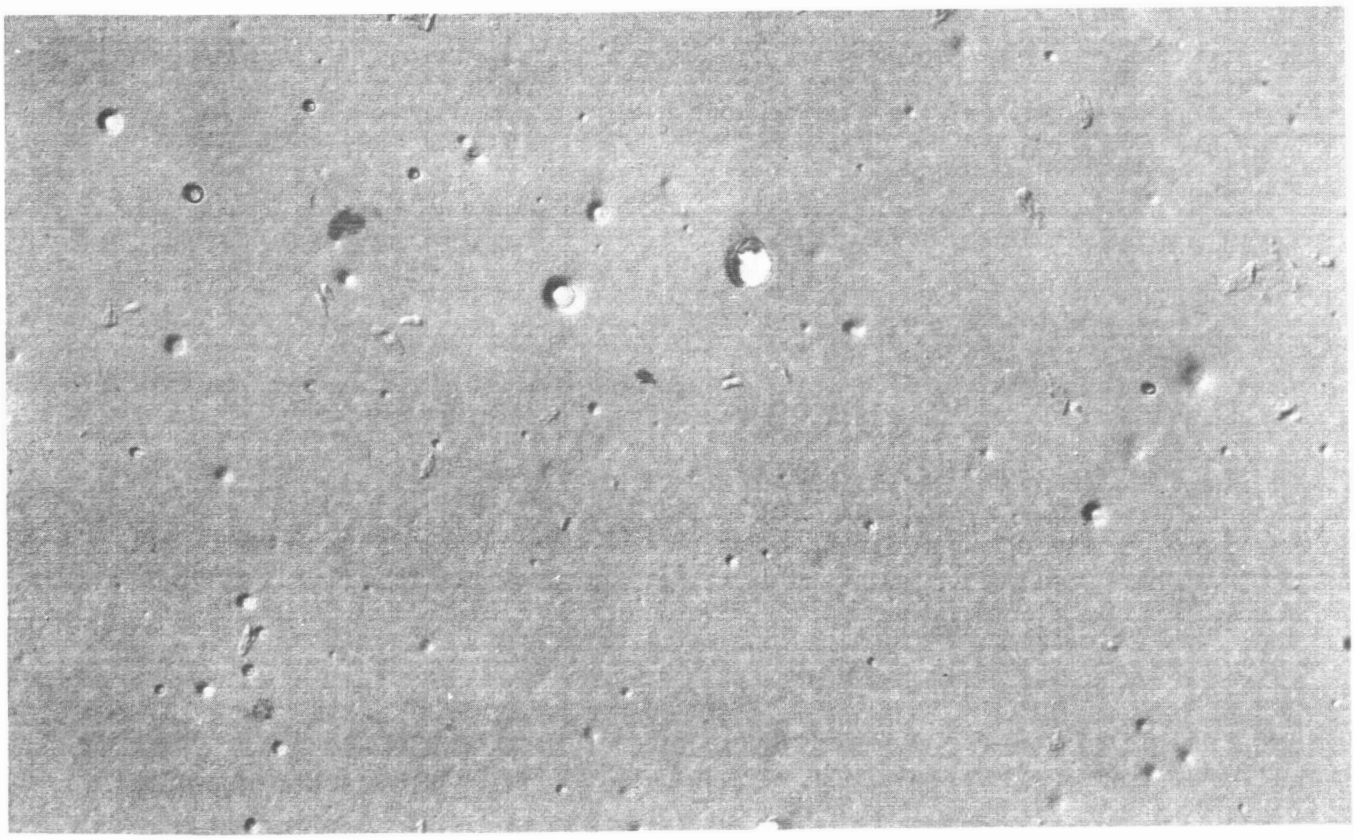
Long period, l, vs annealing temperature (time = 5 hrs.)





Long period, l, vs annealing time at 141°C.





Top Fig. 6. Spherulites of PET crystallized by annealing from a glassy film at about 154°C. Lamellar ribbons are present. Magnification: 86,000X

Bottom Fig. 7. Surface replica of a glassy film before annealing. (pt-C shadowed at $\tan^{-1}$ 5/7) Magnification: 19,200X